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Cite as: AIP Conference Proceedings **1915**, 040032 (2017); https://doi.org/10.1063/1.5017380
Published Online: 12 December 2017

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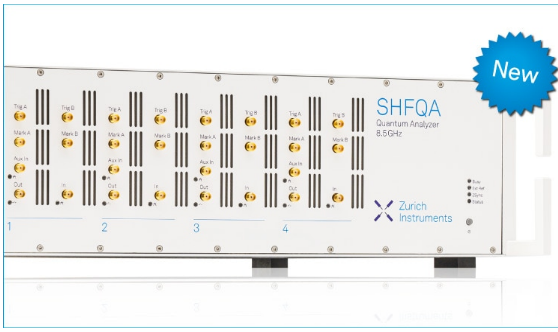

Evolution of Surface Defects in Platinum Alloy Wire under Drawing

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Abstract. The shape and chemical composition of particles polluting the surface of ultrafine wire made of the platinum Pt92.5Pd4Rh3.5 alloy has been revealed by electron microscopy and microspectral analysis. The phenomenon of the appearance of pores in the particles, which are elongated in the direction of drawing, has been discovered. The problem of calculating the stress-strain state is stated by the finite element method. After solving the problem, it is demonstrated that the appearance of additional defects is related to the proportion of stresses in the scheme of metal forming by drawing.

INRODUCTION

Platinum alloy wire is widely used in chemical industry as an element of networks serving as catalysts in various reactions. As the wire diameter decreases in the process of drawing, there appear problems caused by the behavior of defects of various origin. There is defect formation localized inside the wire [1, 2] in the form of metal discontinuities (central bursts, chevron cracks), which is caused by the effect of tensile stresses. This phenomenon depends on the drafting conditions, friction stresses and deformation non-uniformity governed by drawing tool geometry [3]. At certain stress-strain ratios, cracks and irregularities appear on the wire surface rather than in the center, the development mechanism being reported in [4, 5].

Inclusions, i.e. particles of a foreign material introduced in the metal are an additional source of imperfection. They may be located closer to the wire axis, the consequences being analyzed in [6, 7], and near the surface, this being discussed in [8, 9]. Additionally, the properties of an intermediate product are conditioned by inclusion-type defects located at random in the workpiece volume [10]. The aim of this study is to describe the behavior of microdefects in drawing wire made of Pt92.5Pd4Rh3.5 commercial platinum alloy.

EXPERIMENTAL PROCEDURE

Pt92.5Pd4Rh3.5 alloy wire was produced according to the following manufacturing scheme:

- furnace burdening, melting in a 1600 cm^3 crucible; platinum according to GOST 13498, rhodium powder according to GOST 31290, palladium according to GOST 31291, conditioned wastes of platinum, palladium, rhodium and platinum-palladium, platinum-rhodium, platinum-palladium-rhodium alloys are used in alloy smelting; the crucible is made of magnesium oxide or zirconium oxide, up to 1600 cm^3 in volume; first air melting and, after charging all the components, vacuum melting, $(1 \div 8) \cdot 10^{-1}$ mm Hg;
- melt overheating by 100 °C from the melting temperature and followed by casting over the crucible edge into a steel mould;
- gouging of the workpiece on two sides aimed at removing possible inclusions of the crucible material;

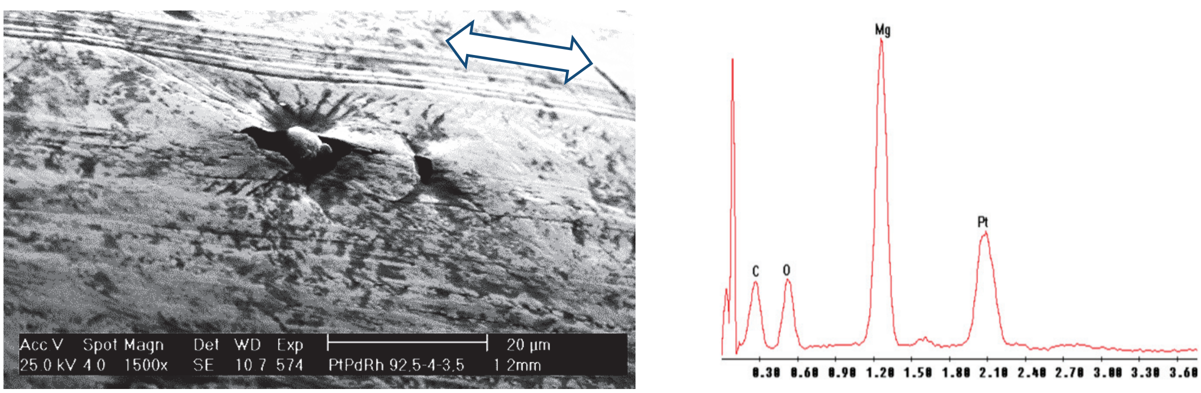
Mechanics, Resource and Diagnostics of Materials and Structures (MRDMS-2017)
AIP Conf. Proc. 1915, 040032-1–040032-4; https://doi.org/10.1063/1.5017380
Published by AIP Publishing. 978-0-7354-1607-9/$30.00

- rod forging by a pneumatic hammer into a plate sized 25×90×L mm (where L is workpiece length), sinkhead removal, checking, cutting the remaining ingot into parts weighing 3500 to 4500 g and forging of square bars sized 27_{-3}×27_{-3}×L mm;
- oval-round bar rolling to a diameter of 8.0 mm;
- drawing to a diameter of 0.092 mm,
- annealing in a continuous electric furnace;
- drawing to a diameter of 1.2 mm;
- annealing in a chamber electric furnace;
- net weaving and shaping.

As soon as the diameter of 1.2 mm was achieved in drawing, the surface of the deformed wire was examined by electron microscopy and microspectral analysis with the use of a Philips XL-30 electron raster microscope with an X-ray micro analyzer.

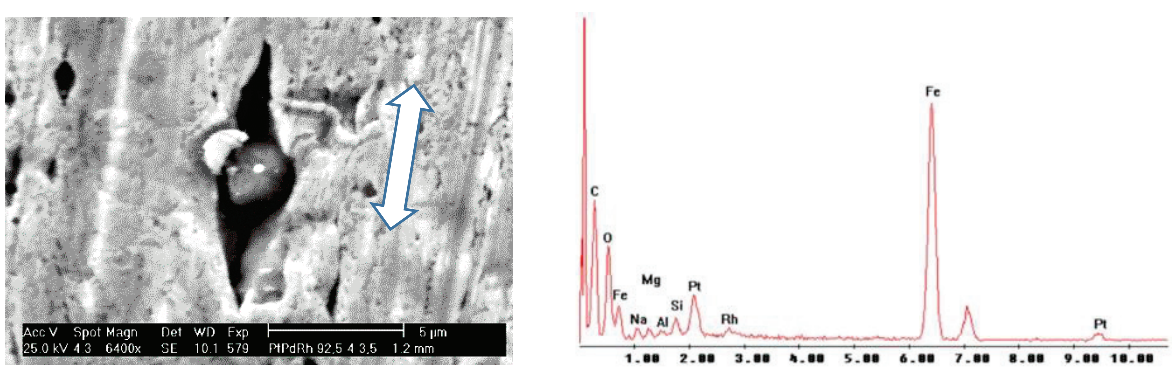
Figure 1 shows a defect in the form of a magnesium-oxide-based ceramic inclusion on the wire surface (*a*) and a spectrogram of the defect and its neighborhood (*b*).

The magnesium-oxide particle gets onto the wire surface due to a partial destruction of the lining of the melting-cutting equipment. This often occurs in casting processes. Figure 2 shows an iron-based almost round particle. If its size is compared with the scale, its plane size proves to be 2 µm; however, the presence of this particle on the surface causes the appearance of an additional defect in the form of two elongated voids, over 8 µm in the total length, adjoining the particle surface. Thus, the presence of inclusions gives rise to other defects, whose sizes may several times exceed that of the primary defect.



(a) (b)

FIGURE 1. A magnesium-oxide-based ceramic inclusion on the surface of 1.2 mm wire made of the Pt92.5Pd4Rh3.5 alloy (a), a spectrogram of the defect and its neighborhood (b); the white arrow shows the drawing axis



(a) (b)

FIGURE 2. An iron-based particle on the surface of 1.2 mm wire made of the Pt92.5Pd4Rh3.5 alloy (*a*), a spectrogram of the defect and its neighborhood (*b*); the white arrow shows the drawing axis

As a rule, iron-based particles get onto the surface of a workpiece under rolling due to the formation of wear products from the rolling mill rolls.

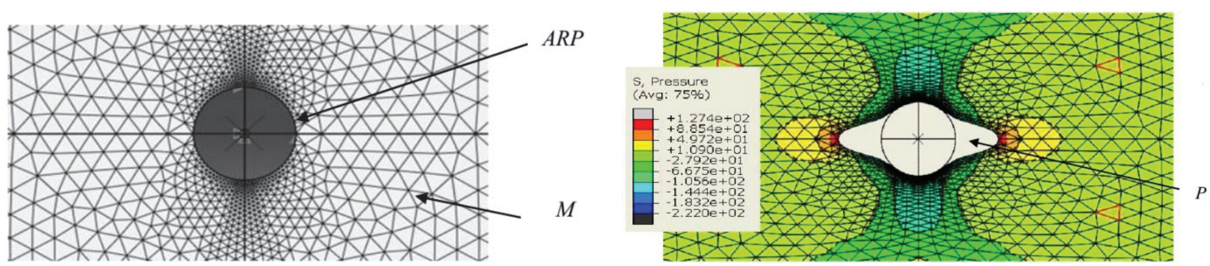
It is obvious from Fig. 1 and 2 that, irrespectively of the material of the particles contaminating the material being processed, there appear pores adjoining the particle surface. The stress pattern under drawing is such that the workpiece metal separates from the particle surface in the direction of rolling, the voids becoming longer from pass to pass. A similar process was discussed in [11, 12] as applied copper oxide particles contained in electrical copper.

CALCULATION PROCEDURE

To determine the forming of the metal near a foreign particle, we apply the Abacus/CAE Student Edition 6.7-2 software package (© Dassault Systemes, Abacus, Inc.). The software version with the number of finite elements under 1000 is used. The wire surface is scanned to turn it into a plane in order to model the defect behavior on this surface. Two objects are examined on the plane, namely, a rectangular fragment of the material being deformed and the round particle of an absolutely rigid material located in the center of the rectangle. The boundary conditions are given in terms of stresses as follows: +400 MPa in the direction of rolling and −300 MPa in the orthogonal direction. The stress signs correspond to the situation of drawing; namely, the axial stresses are tensile and the orthogonal surface (tangential) ones are compressive. The values of stresses are rather conditional since they depend on the tool geometry and the amount of the work hardening of the wire prior to the current drawing pass.

The material properties are specified in the form of a table as the strain dependence of strain resistance or flow stress for the platinum alloy close in chemical composition to that discussed in [13] (nonlinearly hardenable medium). To make the calculations more accurate, we use the symmetry principle saying that the deformation zone is represented as one-fourth of its area located in the first quadrant, the presence of the other fragments being specified in terms of the symmetry boundary conditions. After the problem is solved, the entire deformation zone is restored due to the reflection with respect to the horizontal and vertical axes (Fig. 3).

Surface-to-surface contact boundary conditions, i.e. contact interaction with a possibility of the separation of the material being deformed from the tool surface, are set on the boundary between the plastic and rigid media. On the boundary between the particle and copper, the continuity rule, generally accepted to describe continuous bodies, does not hold. Here, normal metal displacements from the boundary become possible due to the fact that the metal may separate from the boundary and form a void.



(a) (b)

FIGURE 3. Schematic problem solution with a finite element mesh before (*a*) and after (*b*) load application: M – platinum alloy; ARP – absolutely rigid particle; P – void

It follows from Fig. 3 that there are two voids in the horizontal direction with respect to the particle, which are caused by metal separation from its surface. From one loading step to another, the voids stretch in the tensile stress direction. The highest level of strain is revealed for the region of vertical metal compression. Besides, a region with negative pressure values is identified, and this corresponds to positive values of mean (hydrostatic) stress (Fig. 3). These values are observed at the site of metal separation from the particle surface.

When making the calculations, we searched through several variants of the proportion of axial and orthogonal stresses. Particularly, it has been discovered that, when there are stresses of the same sign compression), voids may not appear. This corresponds to the statements of the state-of-the-art theory of metal fracture saying that defect nucleation is favored by a rigid stress pattern, which is implemented when the stress state contains tensile stresses.

Thus, the calculation part of the study verifies the results obtained in the experimental part, namely, drawing of wire with rigid particles on its surface is accompanied by the formation of additional defects of the void type.

CONCLUSION

The process of drawing Pt92.5Pd4Rh3.5 alloy wire is accompanied by the alteration of surface defects. In addition to hard inclusion particles, there appear voids elongated along the direction of drawing. The calculations demonstrate that the growing size of these voids depends on the proportion between the levels of axial and orthogonal stresses.

ACKNOWLEDGMENTS

The work was done within the State Task, theme No. 01201375904, and financially supported by the RF Government, No. 211 (contract No. 02.A03.21.0006).

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